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### Calixarene-supported clusters

**Citation for published version:**

Taylor, SM, McIntosh, RD, Piligkos, S, Dalgarno, SJ & Brechin, EK 2012, 'Calixarene-supported clusters: employment of complementary cluster ligands for the construction of a ferromagnetic  $[Mn_5]$  cage', *Chemical Communications*, vol. 48, no. 91, pp. 11190-11192. <https://doi.org/10.1039/c2cc35944h>

**Digital Object Identifier (DOI):**

[10.1039/c2cc35944h](https://doi.org/10.1039/c2cc35944h)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

Chemical Communications

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Published article available at: <http://dx.doi.org/10.1039/C2CC35944H>

Cite as:

Taylor, S. M., McIntosh, R. D., Piligkos, S., Dalgarno, S. J., & Brechin, E. K. (2012). Calixarene-supported clusters: employment of complementary cluster ligands for the construction of a ferromagnetic [Mn<sub>5</sub>] cage. *Chemical Communications*, 48(91), 11190-11192.

Manuscript received: 16/08/2012; Accepted: 17/09/2012; Article published: 05/10/2012

## Calixarene-Supported Clusters: Employment of Complementary Cluster Ligands for the Construction of a Ferromagnetic [Mn<sub>5</sub>] Cage\*\*

Stephanie M. Taylor,<sup>1</sup> Ruairaidh D. McIntosh,<sup>2</sup> Stergios Piligkos,<sup>3</sup> Scott J. Dalgarno<sup>2,\*</sup>  
and Euan K. Brechin<sup>1,\*</sup>

<sup>[1]</sup>EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

<sup>[2]</sup>Institute of Chemical Sciences, Heriot – Watt University, Riccarton, Scotland, UK.

<sup>[3]</sup>Department of Chemistry, University of Copenhagen, Universitetsparken 5, Denmark.

<sup>[\*]</sup>Corresponding authors; E.K.B. e-mail: [ebrechin@staffmail.ed.ac.uk](mailto:ebrechin@staffmail.ed.ac.uk), fax: +44 (0)131-650-6453, tel: +44 (0)131-650-7545; S.J.D. e-mail: [S.J.Dalgarno@hw.ac.uk](mailto:S.J.Dalgarno@hw.ac.uk), fax: +44 (0)131-451-3180, tel: +44 (0)131-451-8025

<sup>[\*\*]</sup>We thank the EPSRC for financial support of this work ( ref. EP/I031421/1 and EP/H011234/1).

### Supporting information:

†Electronic Supplementary Information (ESI) available: Crystallographic Information File (CIF) and diagrams relating to structure packing and magnetic studies. See <http://dx.doi.org/10.1039/C2CC35944H>

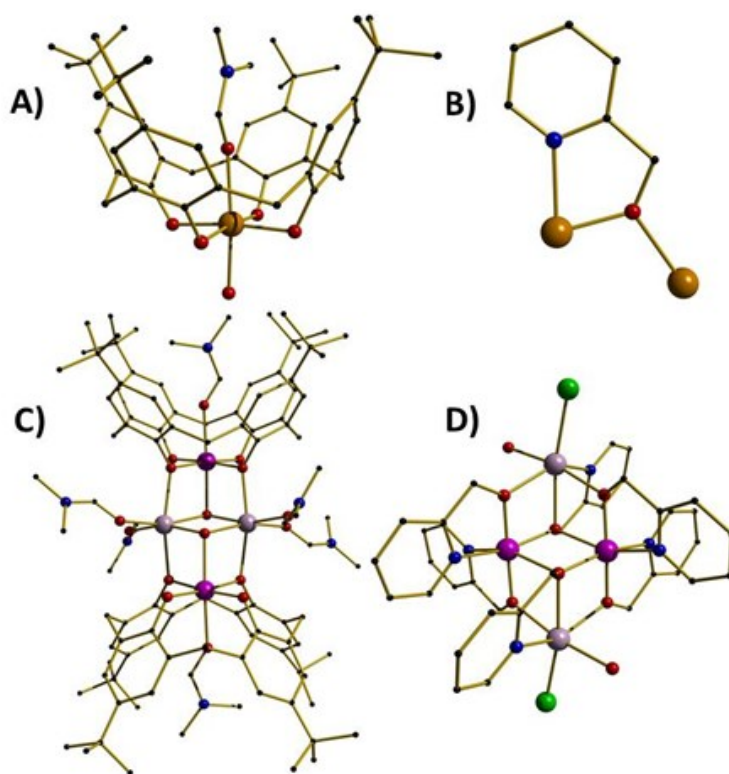
## Abstract

A combination of complementary cluster ligands results in the formation of a new calixarene-supported ferromagnetic  $[\text{Mn}_5]$  cage that displays the characteristic bonding modes of each support.

## Introduction

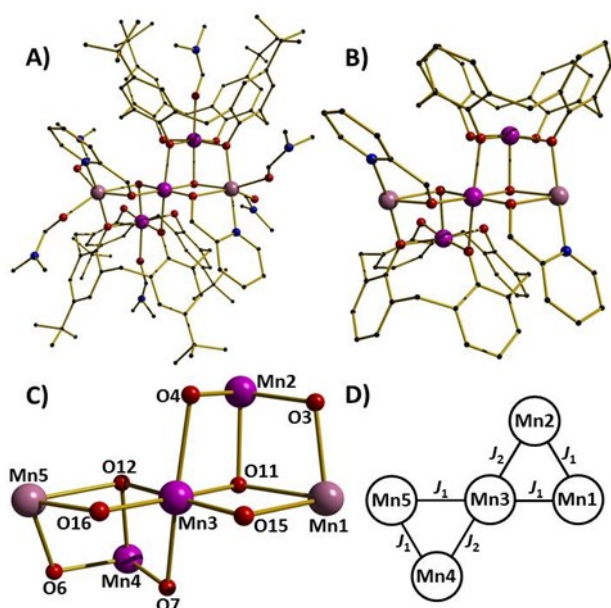
One of the major challenges in the construction of paramagnetic polymetallic cluster compounds is the systematic design and [controlled] assembly of molecules with desirable and/or tuneable magnetic properties.<sup>1-3</sup> This is a non-trivial task since many such species contain high oxidation state metal ions stabilised by a core of bridging oxide and/or hydroxide ions whose presence, number and coordination behaviour is difficult, if not impossible, to control.<sup>1-3</sup> One potential way to circumvent this problem is to take advantage of the known coordination modes of certain ligand types through the self-assembly of complementary cluster ligands, *i.e.* small stable pre-made molecules or metal-organic moieties made *in situ*, that can act as the building blocks from which larger molecules (or indeed coordination polymers) can be made – perhaps even in a logical or step-by-step fashion.<sup>1-3</sup> Of course this approach first requires that a library of complexes, made through (serendipitous) self-assembly, is constructed so that the preferred coordination modes of the ligands with particular metal ions in particular oxidation states, and thus the stable metal building blocks, can be found and exploited.<sup>4</sup> Thereafter one can envision employing different but complementary cluster ligands to build oligomers.

Two appealing classes of ligand in this regard are the *p*-tert-butylcalix[*n*]arenes and the N,O-chelates such as 2-(hydroxy-methyl)pyridine (hmpH), pyridine-2,6-dimethanol (pdmH<sub>2</sub>) and their many derivatives.<sup>5</sup> The *p*-tert-butylcalix[*n*]arenes (TBC[*n*], where *n* indicates the number of aryl units) are cyclic polyphenols that vary in ring size depending on the reaction conditions employed during synthesis.<sup>6</sup> Their polyphenolic nature should make them ideal pro-ligands for the construction of large polynuclear metal clusters, and despite a surprising paucity of early literature examples, we (amongst others) have recently employed TBC[4] as a cluster support with a view to mapping out associated assembly modes and coordination constraints under a range of conditions.<sup>7</sup> Analysis of the common structural features in our TBC[4]-supported clusters shows that whether the calixarene binds a TM<sup>II</sup> (Cu) or TM<sup>III</sup> (Mn or Fe) metal centre, the cavity is occupied by a ligated solvent molecule and the O-atoms of the fully deprotonated lower-rim, in conjunction with a bound hydroxide ligand beneath the complex, act as bridges to other metal centres (Fig. 1A). An appropriate example in the context of the current paper (*vide infra*) is the complex  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{OH})_2(\text{TBC}[4])_2(\text{solvent})_6]$  shown in Figure 1C.<sup>6c</sup>



**Figure 1.** (A) The  $[\text{TM}^{\text{III}}(\text{TBC}[4])(\text{OH})(\text{dmf})]$  cluster ligand. (B) The  $\mu$ -coordination mode commonly found for the  $\text{hmp}^-$  ligand. Colour code for A and B:  $\text{TM}^{\text{III/II}}$  = orange, O = red, N = blue, C = black. (C) Molecular structure of  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{OH})_2(\text{TBC}[4])_2(\text{dmf})_6]$ . (D) Molecular structure of  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{hmp})_6\text{Br}_2(\text{H}_2\text{O})_2]^{2+}$ . Colour code for C and D:  $\text{Mn}^{\text{III}}$  = purple,  $\text{Mn}^{\text{II}}$  = mauve, O = red, N = blue, C = black, Br = green. H-atoms omitted for clarity.

The pro-ligand 2-(hydroxymethyl)pyridine (hmpH) has a proven track record of success in the construction of Mn clusters.<sup>5,8</sup> Typically  $\text{hmp}^-$  acts as a  $\mu$ -bridge, chelating to one Mn centre through N- and O-atoms and bridging to the second metal *via* the alkoxide (Fig. 1B), though the ligand can also act as a  $\mu_3$ -bridge. Perhaps this is best illustrated in the complex  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{hmp})_6\text{Br}_2(\text{H}_2\text{O})_2]^{2+}$  (Fig. 1D) and its analogues.<sup>5</sup> The metal-oxygen core topology in this family is often referred to as a butterfly (two edge-sharing triangles) with the wingtip (outermost)  $\text{Mn}^{\text{II}}$  ions being ferromagnetically coupled to the body (innermost)  $\text{Mn}^{\text{III}}$  ions. This structure is clearly related to that of  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{OH})_2(\text{TBC}[4])_2(\text{dmf})_6]$  shown in Figure 1C and we reasoned that the two cluster ligand moieties / building blocks in Figures 1A and 1B should be complementary and that their simple addition should result in the self-assembly of a structurally related complex. Herein we report the synthesis, structure and initial magnetic properties of the complex  $[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{II}}_2(\text{OH})_2(\text{TBC}[4])_2(\text{hmp})_2(\text{dmf})_6](\text{TBC}[4]\text{-H}) \cdot 2.6(\text{dmf}) \cdot 1.4(\text{H}_2\text{O})$  (**1**) whose structure indeed describes the self-assembly of the moieties shown in Figures 1A and 1B.



**Figure 2.** (A) Molecular structure of the cation in **1**. (B) Molecular structure of the cation in **1** with TBC[4] tert-butyl groups and dmf molecules removed. (C) Metal-oxygen magnetic core of the cation in **1**. (D) Schematic of the metallic skeleton of the cation in **1**, indicating the exchange coupling model employed to fit the susceptibility data. Colour code: Mn<sup>III</sup> = purple, Mn<sup>II</sup> = mauve, O = red, N = blue, C = black. H-atoms omitted for clarity.

The reaction of MnCl<sub>2</sub>·4H<sub>2</sub>O, TBC[4], Hhmp and NEt<sub>3</sub> in a solvent mixture of DMF and EtOH followed by slow evaporation of the mother liquor produces black crystals of **1** in ~50 % yield over 7 days.‡ Crystals of **1** are in a triclinic cell and structure solution was performed in the space group *P*-1, with the asymmetric unit comprising the entire formula listed above.† The metallic skeleton of **1** (Fig. 2) describes two vertex-sharing [Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup>] triangles, with Mn1 and Mn5 being in the II+ oxidation state and Mn2-4 being in the III+ oxidation state. Mn3 is the shared vertex. The two μ<sub>3</sub>-OH<sup>-</sup> ions (O11, O12) lie at the centres of these triangles, but not in the same plane and thus perhaps a more accurate description of the [Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup>(OH)] moiety is that of a partial cubane. The TBC[4] ligands are fully deprotonated and each house a Mn<sup>III</sup> ion in the centre of their phenolic pocket (Mn2, Mn4); two O-atoms (O1, O2 and O5, O8)

are terminally coordinated, but the remaining two (O3, O4 and O6, O7) bridge to the other Mn ions (Mn1, Mn3 and Mn3, Mn5) in the partial cubane. The hmp<sup>-</sup> ions chelate to the Mn<sup>II</sup> ions (Mn1, Mn5) and use their alkoxide arm (O15, O16) to bridge to Mn3. All the Mn ions are six-coordinate, with the remaining sites filled with terminally coordinated dmf molecules: two on each of the Mn<sup>II</sup> ions completing the {MnO<sub>5</sub>N} coordination sphere, and one on Mn2 and Mn4, both of which reside in the hydrophobic calixarene cavities. The coordination spheres of the III+ ions are thus all {MnO<sub>6</sub>}. The

Jahn-Teller axes of the Mn<sup>III</sup> ions are defined by the OH-Mn-DMF vector for Mn2 and Mn4, and by O4(TBC4)-Mn-O7(TBC4) for Mn3, and are thus approximately co-parallel. The  $\mu_3$ -OH<sup>-</sup> ions are H-bonded to the terminally bonded O-atoms of the TBC[4] ligands (O...O, ~2.8 Å), with the latter also H-bonded to H<sub>2</sub>O molecules of crystallisation (O...O, ~2.8 – 2.9 Å). Charge balance is maintained through the presence of one (TBC[4]-H)<sup>-</sup> anion per Mn<sub>5</sub> cluster. In our previous studies using TBC[4] as a cluster support<sup>6b-e</sup> we have observed a propensity for these systems to assemble in a manner akin to the solvates of the calixarene (in anti-parallel bi-layer arrays).<sup>7</sup> The extended structure in **1** is unusual in that it contains an additional TBC[4] that is present as a mono-anion. This [TBC4-H] anion co-crystallises orthogonal to the cation, with a DMF of crystallisation occupying the calixarene cavity (Fig. S1). An inevitable result of this packing is that the components are unable to form the expected bi-layer array. Despite this feature, symmetry equivalent cations are still arranged in a manner which is reminiscent to the dmf solvate of TBC[4] in so far as the upper-rim tert-butyl groups are still arranged head-to-head in layers (Fig. S2).<sup>6b</sup> Neighbouring clusters are generally found to be isolated, interacting primarily through two crystallographically unique CH...O interactions (distances of 2.864 & 2.938 Å) between an hmp ligand and a symmetry equivalent dmf ligand.

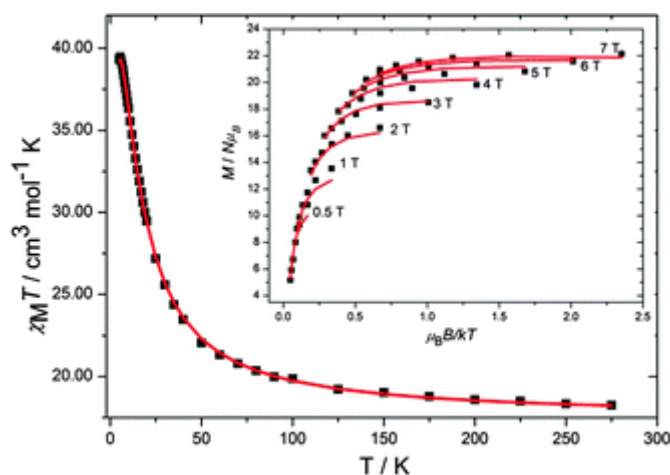
Solid state dc magnetic susceptibility measurements were carried out on polycrystalline samples of **1** in the 275-5 K temperature range in an applied field of 0.1 T (Figure 3). The high temperature  $\chi_M T$  value of 18.6 cm<sup>3</sup> K mol<sup>-1</sup> is close to the spin-only value expected for an uncoupled [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup><sub>2</sub>] unit of 17.75 cm<sup>3</sup> K mol<sup>-1</sup> with  $g = 2.0$ . The  $\chi_M T$  value then increases slowly with decreasing temperature reaching a value of approximately 20.3 cm<sup>3</sup> K mol<sup>-1</sup> at 100 K, below which it then increases more rapidly reaching a maximum value of ~40.3 cm<sup>3</sup> K mol<sup>-1</sup> at 5.5 K. This behaviour is suggestive of weak intramolecular ferromagnetic exchange.

$$\hat{H} = -2[J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_4 \cdot \hat{S}_5) + J_2(\hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4)] \quad (1)$$

$$+ D_{Mn} \sum_{i=2,3,4} \{\hat{S}_{z,i}^2 - S(S+1)/3\} + \mu_B g \vec{B} \cdot \sum_{i=1}^5 \{\hat{S}_i\}$$

The experimental  $\chi_M T$  data of **1** can only be fitted by use of the anisotropic spin-Hamiltonian model (1), depicted in Figure 2D;<sup>9</sup> where  $J_1$  and  $J_2$  are the Mn<sup>III</sup>-Mn<sup>II</sup> and Mn<sup>III</sup>-Mn<sup>III</sup> isotropic exchange parameters, respectively,  $\hat{S}$  is a spin-operator,  $i$  runs from 1 to 5,  $D$  is the single-ion axial anisotropy parameter of Mn<sup>III</sup>,  $\mu_B$  is the Bohr magneton,  $\vec{B}$  is the applied magnetic field vector, and  $g = 2.00$  is the  $g$ -factor of the Mn ions. In addition, intermolecular interactions were taken into account through the introduction of the Curie- Weiss temperature,  $\theta$ . The resulting best-fit curve, obtained by full matrix diagonalisation of the full spin-Hamiltonian matrix of dimension 4500, is shown as the solid red line in Figure 3. The best fit parameters obtained from fitting the  $\chi_M T$  data are  $J_1 = +0.348$  cm<sup>-1</sup>,  $J_2 = +2.553$  cm<sup>-1</sup> and  $D = -2.267$  cm<sup>-1</sup> and  $\theta = -1.64$  K. Taking into account the zero-field isotropic part of spin-Hamiltonian (1) and with these parameters, the ground spin-state of the system is an  $S = 11$  state.

The full zero-field, isotropic, energy spectrum of **1** is given in Figure S3. The magnitude of the exchange interactions resembles that observed for both  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{OH})_2(\text{TBC}[4])_2(\text{solvent})_6]$  and  $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{hmp})_6\text{Br}_2(\text{H}_2\text{O})_2]^{2+}$ . To better estimate  $D$ , we modelled the variable-field and variable-temperature magnetisation data of **1** in the temperature range 2 to 7 K and in applied fields from 0.5 to 7.0 T (Figure 3, inset). We again used spin-Hamiltonian (1) and the Levenberg-Marquardt algorithm,<sup>9</sup> with  $J_1$  and  $J_2$  fixed and only fitted  $D$  and  $\theta$ . The resulting best-fit parameters were  $D = -2.111 \text{ cm}^{-1}$  and  $\theta = -0.080 \text{ K}$ , reflecting that the intermolecular interactions are quenched by high magnetic fields. Ac susceptibility studies carried out on crystalline samples of **1** in the 1.8-10.0 K range in a 3.5 G field oscillating at frequencies up to 1000 Hz (Figure S4) display frequency-dependent out-of-phase ( $\chi_M''$ ) signals suggestive of SMM behaviour. An Arrhenius plot constructed from these data afford  $U_{\text{eff}} = 42 \text{ K}$  with  $\tau_0 = 1.125 \times 10^{-10} \text{ s}$ .



**Figure 3.** A) Plot of the  $\chi_M T$  product of **1** vs.  $T$  in the 275 - 5 K temperature range in an applied field of 0.1 T. The solid red line is the best-fit of the data. Inset: Plot of reduced magnetisation in the 2.0 to 7.0 K temperature range and at the indicated field strengths. The solid red lines are the best-fit of the data. See text for details.

In conclusion we have shown that the use of complimentary cluster ligands is an excellent method for cluster growth; in this case the combination of *p*-tert-butylcalix[4]arene and 2-(hydroxymethyl)pyridine produces a ferromagnetic  $[\text{Mn}_5]$  cage that displays the characteristic bonding modes of each support. This would suggest that an in-depth search of the CCDC database may reveal other hitherto untried ligand combinations that would result in molecules with interesting structural and/or magnetic characteristics.

## Notes and references

### ‡Synthesis of $[\text{Mn}^{\text{III}}_3\text{Mn}^{\text{II}}_2(\text{OH})_2(\text{TBC}[4])_2(\text{hmp})_2(\text{dmf})_6](\text{TBC}[4]\text{-H})\cdot 2.6(\text{dmf})\cdot 1.4(\text{H}_2\text{O})$ , **1**:

$\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  (0.12 g, 0.6 mmol), Hhmp (0.065 g, 0.6 mmol) and TBC4 (0.2g, 0.3 mmol) were dissolved in a mixture of MeOH ( $10\text{ cm}^3$ ) and DMF ( $10\text{ cm}^3$ ). After 5 minutes of stirring,  $\text{NEt}_3$  (2.5 ml, 1.8 mmol) was added, leaving the solution stirring for a further 2 h. Black single crystals suitable for diffraction studies were obtained by slow evaporation of the mother liquor over a period of 1 week in ~50 % yield. The complex can also be obtained in similar yield from mixing separate solutions of  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ , TBC4 and  $\text{NEt}_3$  in MeOH/DMF with  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ , Hhmp and  $\text{NEt}_3$  in MeOH/DMF. Elemental analysis (%) calculated (found) for  $\text{Mn}_5\text{C}_{162}\text{H}_{217}\text{O}_{22}\text{N}_8$  (2903.24): C 67.02 (67.34), H 7.53 (7.95), N 3.86 (4.24). **Crystal Data for 1:**  $\text{C}_{169.80}\text{H}_{236}\text{Mn}_5\text{N}_{10.60}\text{O}_{26}$ ,  $M = 3116.39$ , Black Block,  $0.45 \cdot 0.35 \cdot 0.30\text{ mm}^3$ , triclinic, space group  $P-1$  (No. 2),  $a = 19.5877(9)$ ,  $b = 21.2285(10)$ ,  $c = 22.6548(10)\text{ \AA}$ ,  $\alpha = 100.189(2)$ ,  $\beta = 110.810(2)$ ,  $\gamma = 102.360(2)^\circ$ ,  $V = 8265.0(7)\text{ \AA}^3$ ,  $Z = 2$ , Bruker X8 Apex II CCD Diffractometer,  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ),  $T = 100(2)\text{K}$ ,  $2\theta_{\text{max}} = 54.2^\circ$ , 129252 reflections collected, 35410 unique ( $R_{\text{int}} = 0.0312$ ). Final  $\text{Goof} = 1.046$ ,  $R_1 = 0.0593$ ,  $wR_2 = 0.1370$ ,  $R$  indices based on 26610 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ).

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